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SOLUTION AND ADSORPTION THERMODYNAMICS IN PROPYLENE GLYCOL BY GAS CHROMATOGRAPHY

A COMPARATIVE STUDY WITH OTHER POLYHYDROXYLATED SOLVENTS

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SUMMARY

The retention volumes of eighteen hydrocarbons representative of different families and of acetone, diisopropyl ether and three chloromethanes were measured at four temperatures within the range 12–22°C on columns containing five different percentages of propylene glycol (PG) as the stationary phase. The relative magnitudes of the adsorption on PG, on formamide and on four glycols are compared and discussed in terms of the thermodynamic properties of the bulk mixtures with hydrocarbons. From this comparison, PG is found to possess the weakest adsorption effects, and some of the solutes studied exhibit no adsorption within experimental error. The thermodynamic properties of solution in PG are calculated and compared to those in formamide and in the glycols. Recent extensions of the regular solutions model are inefficient for calculating infinite dilution activity coefficients, but yield a very acceptable correlation between heats of solution and solute solubility parameters.

INTRODUCTION

The use of gas chromatography (GC) to study the solution and adsorption thermodynamics of hydrocarbons in polar solvents has been reported in previous papers. The solvents studied included formamide (FA)¹, di- and triethylene glycol (DEG, TEG)², ethylene glycol (EG)³ and glycerol (GLY)⁴. Some of these are employed in petrochemical separation processes, and the others are potentially inter-

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esting. The measurement of the activity coefficients of hydrocarbons of different families at infinite dilution constitutes an excellent gauge when comparing their selectivities and capacities⁵. Moreover, these solvents are very structured liquids, only surpassed by water, and the study of the thermodynamics of their mixtures with hydrocarbons can be of great help in the understanding of aqueous solutions of non-electrolytes, a topic of great biological importance⁶.

Chromatographic retention in these systems is the result of simultaneous processes of partition and adsorption on the gas-liquid interface. The net retention volume per gram of packing, V_N° , can thus be expressed by Martin's equation^{7,8}

$$V_N^\circ = K_L V_L^\circ + K_A A_L^\circ \quad (1)$$

where K_L is the liquid-gas partition coefficient and K_A is the adsorption coefficient at the gas-liquid interface; V_L° is the liquid volume and A_L° is the liquid surface area, both expressed per gram of packing.

In the present work the results obtained with 1,2-propanediol (propylene glycol, PG) as the stationary phase and a series of hydrocarbons and a small number of other substances as solutes are presented. The behaviour of PG is then compared to those of the other polar stationary phases, in an attempt to understand and to systematize their properties.

EXPERIMENTAL

The apparatus used and the procedure followed were as previously described^{1,2}. Retention volumes were measured at four temperatures within the range 12–22°C. Analytical grade nitrogen was employed as carrier gas; flow-rates in the range 15–60 cm³/min were chosen to give adequate retention times.

PG was Carlo Erba RS for chromatography, purified by percolation through a column packed with molecular sieve 4A; the final product contained 0.04% of water, as determined by the Karl Fischer technique. The 23 solutes studied, all more than 99% pure, were of different origins and were used as received.

Chromosorb P (60–80 mesh), acid washed, was used as the solid support. The columns were made from 0.25 in. O.D. stainless-steel tubing, in two different lengths: 25 cm for aromatic hydrocarbons, *n*-nonane, acetone and chloroform, and 50 cm for the remaining solutes. The characteristics of the columns are given in Table I. In order to attain constancy in the retention times, the columns had to be preconditioned with a small flow of dry nitrogen at room temperature for 24 h. A precolumn packed with the same packing as the analytical column was employed in all the experiments.

RESULTS

Net retention volumes, V_N , were calculated from the expression

$$V_N = F^o j t'_R \quad (2)$$

where F^o is the volumetric flow-rate at the column temperature and outlet pressure, j is the James-Martin carrier-gas compressibility correction factor and t'_R is the ad-

TABLE I
COLUMN CHARACTERISTICS

W = Amount (g) of total packing in the column; V_L = volume (cm³) of PG per gram of packing at 17°C; A_L = area (cm²) of liquid surface exposed per gram of packing.

<i>Column length: 25 cm</i>					
PG (% w/w)	5.160	8.010	11.59	14.38	16.74
W	1.675	1.794	1.753	1.815	1.945
V_L	0.0497	0.0771	0.1116	0.1385	0.1612
A_L	12,950	11,060	8730	7350	6350
<i>Column length: 50 cm</i>					
PG (% w/w)	4.786	7.483	9.335	12.10	15.24
W	3.4782	3.651	3.709	3.714	3.880
V_L	0.0460	0.0721	0.0899	0.1166	0.1468
A_L	13,300	11,480	10,390	8660	7030

justed retention time. The experimental values obtained on each column were fitted to equations of the type

$$\ln V_N = -\Delta H_s/RT + \text{constant} \quad (3)$$

where the meaning of ΔH_s , the heat of sorption, depends on the operating retention mechanism. Experimental and interpolated values of V_N differed by at most 0.7%.

The solutes under study exhibit two different types of behaviour, as revealed by plots of V_N° against the percentage of stationary phase. Alkanes, olefins, diisopropyl ether and ethylcyclohexane are retained by partition and adsorption on the gas-liquid interface, with the adsorption contribution decreasing in the mentioned sequence. Retention of the remaining solutes can be explained, within experimental error, exclusively in terms of solution in the stationary phase.

Partition and adsorption coefficients for the adsorbable solutes were obtained from the slopes of the straight line plots of V_N°/A_L° against V_L°/A_L° and of V_N°/V_L° against A_L°/V_L° , respectively; the estimation of A_L° was detailed in a previous publication¹, and the values of V_L° were calculated using Riddick and Bunger's compilation⁹ of data on PG density at different temperatures. The values of K_L and K_A in the middle of the experimental temperature range (17°C) are given in Tables II and III, respectively, together with their 95% confidence intervals computed from the standard deviations of the slopes.

In the case of solutes retained exclusively by solution in the stationary phase, a partition coefficient was calculated for each column by means of the relation $K_L = V_N^\circ/V_L^\circ$. The values of K_L for these solutes in Table II are the averages of the results obtained on the five columns, and the 95% confidence intervals were computed from the standard deviations.

The standard molar enthalpies of solution, ΔH_s° , reported in Table II were calculated following Meyer's proposal¹⁰, and correspond to the transfer of one mole of solute from an ideal vapour phase at a pressure of 1 atm to a hypothetical solution at unitary molar fraction and obeying Henry's law. The precision of the enthalpies of solution was estimated as described by Castells¹¹ in the case of solutes retained by mixed mechanisms, and from the standard deviations of the slopes of plots of

TABLE II

THERMODYNAMIC FUNCTIONS OF SOLUTION OF VAPOURS IN PROPYLENE GLYCOL AT 17°C

<i>Solute</i>	K_L	$-\Delta H_k^\circ$ (kcal/mol)	$-\Delta H_L^\circ$	$\gamma_1^{b,\infty}$	$-\bar{S}_1^\circ$ (cal/°K) · mol)
1 <i>n</i> -Hexane	28.3 ± 0.5	7.2 ± 0.3	7.7	82.6	7
2 <i>n</i> -Heptane	66.0 ± 1.0	8.2 ± 0.2	8.9	124	7
3 <i>n</i> -Octane	150 ± 3	8.9 ± 0.3	10.1	188	6
4 <i>n</i> -Nonane	335 ± 6	9.3 ± 0.3	11.1	294	5
5 Isooctane	54.8 ± 0.9	7.9 ± 0.2	8.6	136	8
6 1-Hexene	37.2 ± 0.8	7.2 ± 0.3	7.5	50.6	7
7 1-Heptene	87.6 ± 2.2	8.2 ± 0.3	8.7	74.8	7
8 1-Octene	198 ± 5	8.8 ± 0.3	9.9	113	6
9 Cyclohexane	88.3 ± 1.5	7.4 ± 0.2	8.0	41.6	5
10 Methylcyclohexane	134 ± 5	7.9 ± 0.4	8.6	59.2	6
11 Ethylcyclohexane	325 ± 6	8.8 ± 0.3	9.8	94.0	6
12 Cyclohexene	149 ± 4	7.5 ± 0.2	8.1	27.2	4
13 Benzene	295 ± 7	7.7 ± 0.2	8.2	12.9	3
14 Toluene	665 ± 11	8.6 ± 0.2	9.2	20.0	4
15 Ethylbenzene	1390 ± 20	9.6 ± 0.1	10.2	29.7	5
16 <i>p</i> -Xylene	1410 ± 28	9.6 ± 0.2	10.2	31.8	5
17 <i>m</i> -Xylene	1450 ± 30	9.7 ± 0.2	10.3	32.7	5
18 <i>o</i> -Xylene	2010 ± 51	9.9 ± 0.2	10.5	29.8	5
19 Diisopropyl ether	121 ± 3	7.7 ± 0.3	7.9	20.2	5
20 Acetone	416 ± 4	6.9 ± 0.1	7.6	3.68	0
21 Carbon tetrachloride	228 ± 2	8.2 ± 0.1	8.1	14.4	6
22 Chloroform	557 ± 11	8.9 ± 0.2	7.5	3.23	7
23 Dichloromethane	207 ± 2	7.6 ± 0.1	6.9	3.81	5

In K_L against T^{-1} for solutes retained exclusively by partition. Latent heats of condensation at 17°C, ΔH , were taken from Dreisbach's compilation^{12,13}.

TABLE III

ADSORPTION COEFFICIENTS AND SURFACE ACTIVITY COEFFICIENTS OF VAPOURS ON PROPYLENE GLYCOL AT 17°C

<i>Solute</i>	$10^5 \cdot K_A$ (cm)	$\gamma_1^{a,\infty}$
1 <i>n</i> -Hexane	3.70 ± 0.44	15.3
2 <i>n</i> -Heptane	9.37 ± 0.87	20.1
3 <i>n</i> -Octane	29.7 ± 1.9	21.7
4 <i>n</i> -Nonane	66.7 ± 4.6	32.6
5 Isooctane	12.1 ± 0.74	19.2
6 1-Hexene	3.30 ± 0.67	12.9
7 1-Heptene	8.27 ± 1.8	17.2
8 1-Octene	28.6 ± 2.8	16.8
11 Ethylcyclohexane	20.5 ± 3.4	19.4
19 Diisopropyl ether	9.3 ± 2.0	7.15

The activity coefficients at infinite dilution in the bulk phases were calculated by the equation

$$\gamma_1^{b,\infty} = RT/p_1^{\circ}v_2 K_L \quad (4)$$

where p_1° is the saturation vapour pressure of the solute, obtained from Dreisbach's tables, and v_2 is the molar volume of the stationary phase.

DISCUSSION

When the properties of propylene glycol as a stationary phase are compared with those of related compounds, the small magnitude of the adsorption effects stands out as the most important difference. Some properties of the systems of four representative hydrocarbons with PG, GLY, EG, DEG, TEG and FA are compared in Table IV.

It is usually stated that adsorption increases with increasing positive deviations from Raoult's law. The ratio K_A/K_L can be taken as a gauge to compare the relative magnitudes of adsorption, and Martire¹⁴ found a quasi-linear relationship between K_A/K_L and $\gamma_1^{b,\infty}$ for several solutes with thiodipropionitrile as stationary phase. However, there are many exceptions to this rule. Thus diisopropyl ether exhibits a relatively strong adsorption on PG, with a K_A/K_L value of 8×10^{-7} cm at 25°C, comparable to 10×10^{-7} cm for 1-heptene; but the activity coefficient of diisopropyl ether is almost coincident with that of toluene, which exhibits no measurable adsorption. The activity coefficients of the hydrocarbons at infinite dilution are higher in PG than in TEG, but the values of K_A/K_L are consistently higher for TEG. The adsorption of *n*-

TABLE IV

COMPARISON OF ADSORPTION AND SOLUTION PROPERTIES OF REPRESENTATIVE HYDROCARBONS IN SEVERAL STATIONARY PHASES AT 25°C

Solute	Parameter	Stationary phase and surface tension (dyn/cm)					
		GLY	EG	PG	DEG	TEG	FA
		62.5	46.0	36.5	44.8	45.1	57.9
<i>n</i> -Heptane	$\gamma_1^{b,\infty}$	2030	1020	120	166	98.5	2200
	$10^5 \cdot K_A$ (cm)	18.9	13.4	6.81	23.4	26.9	13.9
	$10^7 \cdot K_A/K_L$ (cm)	690	188	14.8	90.9	87.0	303
1-Heptene	$\gamma_1^{b,\infty}$	1380	507	73.4	83.5	49.5	1010
	$10^5 \cdot K_A$ (cm)	19.8	14.0	6.12	24.8	28.4	16.2
	$10^7 \cdot K_A/K_L$ (cm)	602	120	10.0	59.5	56.8	198
Cyclohexane	$\gamma_1^{b,\infty}$	1250	253	41.7	50.9	30.8	492
	$10^5 \cdot K_A$ (cm)	6.08	4.75	1.27	8.03	8.62	4.76
	$10^7 \cdot K_A/K_L$ (cm)	293	35.5	2.05	20.5	18.8	49.0
Benzene	$\gamma_1^{b,\infty}$	131	32.3	12.6	6.48	3.80	52.3
	$10^5 \cdot K_A$ (cm)	9.64	8.94	(3.19)*	10.1	8.58	9.47
	$10^7 \cdot K_A/K_L$ (cm)	47.2	8.26	(1.51)*	3.19	2.24	10.1

* Calculated from Fig. 1.

heptane on GLY is more than twice as much as that of *n*-heptane on FA, in spite of a slightly larger activity coefficient in this last solvent; *n*-octane and *n*-nonane exhibit the same trend.

By applying Gibbs' model of the interface, Eon and Guiochon¹⁵ arrived at the expression

$$K_A = K_L \frac{v_2}{a_2} \left\{ \frac{\gamma_1^{b,\infty}}{\gamma_1^{s,\infty}} \cdot \exp \left[\frac{a_1(\sigma_2 - \sigma_1)}{RT} \right] - 1 \right\} \quad (5)$$

where $\gamma_1^{s,\infty}$ is the surface activity coefficient at infinite dilution, defined by analogy with its bulk counterpart, $\gamma_1^{b,\infty}$; v_2 , a_2 and σ_2 are the molar volume, molar surface area and surface tension, respectively, of the pure stationary phase; σ_1 and a_1 represent the surface tension and molar surface area of the solute. This equation provides a sounder basis for the correlation of K_A values, as differences in surface tension and molar surface area are taken into consideration. For high values of the stationary phase surface tension the exponential term in eqn. 5 is of the utmost importance in determining the value of K_A , and affords an interpretation of the discrepancies mentioned in the preceding paragraph. Thus, the surface tension of diisopropyl ether is only 17.3 dyn/cm, against 27.9 dyn/cm for toluene; PG has a lower surface tension than TEG, and the surface tension of FA is considerably lower than that of GLY (see Table IV).

However, from the point of view of predicting K_A values, eqn. 5 is of little help, as our ignorance of K_A has been transferred to $\gamma_1^{s,\infty}$. Adsorption on the gas-liquid interface will be noticeable with stationary phases of high surface tension, the most common case being that of a highly polar, probably associated liquid. Activity coefficients in mixtures with this type of solvents, whether in the bulk or in surface phases, cannot be predicted by means of the present theories of non-electrolyte mixtures.

Nevertheless, for systems where K_A and K_L have been measured in the form originally proposed by Martin^{7,8}, both $\gamma_1^{b,\infty}$ and $\gamma_1^{s,\infty}$ can be calculated through eqns. 4 and 5. Such calculations have been performed for several hydrocarbons with thiodipropionitrile, FA, EG, DEG and TEG¹⁶ and with GLY⁴, yielding linear plots of $\ln \gamma_1^{s,\infty}$ against $\ln \gamma_1^{b,\infty}$ for a given stationary phase, with correlation coefficients higher than 0.95. Furthermore, a good correlation was found between the enthalpies of adsorption and the enthalpies of solution, suggesting that non-idealities in both phases are the outcome of the same group of factors.

Fig. 1 shows a plot of $\ln \gamma_1^{s,\infty}$ vs. $\ln \gamma_1^{b,\infty}$, at 17°C, for the solutes that exhibit a measurable adsorption effect on PG. The straight line was drawn through the experimental points by the least squares method, and the correlation coefficient is 0.972. If we assume that the points corresponding to solutes that (within experimental error) do not exhibit adsorption effects fall on the same line, Fig. 1 can be employed to evaluate the surface activity coefficients of this group of solutes and then, through eqn. 5, their adsorption coefficients. By using these K_A values it is possible to compute the per cent contribution of adsorption to the total retention volume. The resulting contributions are smaller than 6% on the columns with the lowest stationary phase loadings (around 5%, w/w), falling to less than 1% for columns with more than 10%

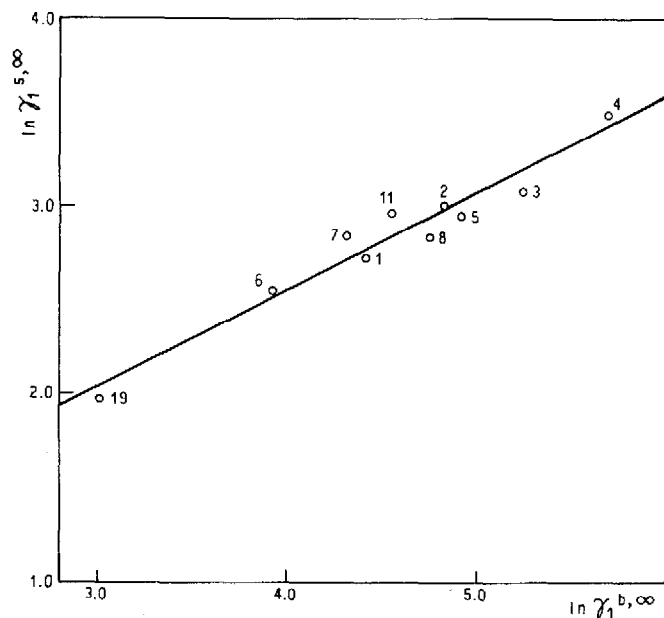


Fig. 1. Surface and bulk activity coefficients in propylene glycol at infinite dilution and 17°C. Solute numbers as indicated in Table II.

of stationary phase. To measure such a feeble adsorption effect, a solid support yielding exposed stationary phase specific surface areas approximately ten times higher than those obtained with Chromosorb P would have to be used.

Due to the low adsorption contribution exhibited by PG columns, the confidence intervals of the adsorption coefficients in Table III are very wide. The enthalpies of adsorption computed from these coefficients will be affected by errors of the order of 1 kcal/mol, and in consequence have been omitted from Table III.

For the same reasons, the precision of the partition coefficients is obviously higher, yielding solution enthalpies with uncertainties of only ± 0.1 – 0.3 kcal/mol. Partial molar excess properties of solution can be computed by means of the following equations¹⁰:

$$\bar{G}_1^e = RT \ln \gamma_1^{b, \infty} \quad (6)$$

$$\bar{H}_1^e = \Delta H_k^e - \Delta H_L^e \quad (7)$$

$$\bar{S}_1^e = (\Delta H_k^e - \Delta H_L^e)/T - R \ln \gamma_1^{b, \infty} \quad (8)$$

The excess entropies thus calculated are given in Table II; the values for all of the solutes are negative and, with the exception of acetone, relatively high.

It is probably pertinent to mention here that the same type of result is obtained for solutions of hydrocarbons in FA¹, EG³, DEG and TEG² and GLY⁴. A group of representative results is collected in Table V, together with the excess entropies of benzene and toluene in water, taken for comparative purposes from a paper by Karger *et al.*¹⁷.

TABLE V

PARTIAL MOLAR EXCESS ENTROPIES OF HYDROCARBONS OF DIFFERENT FAMILIES IN SEVERAL SOLVENTS (cal/°K · mol)

Solute	Solvent						
	Water (12.5°C)	Glycerol (25°C)	Ethylene glycol (25°C)	Propylene glycol (17°C)	Diethylene glycol (25°C)	Triethylene glycol (25°C)	Formamide (25°C)
<i>n</i> -Heptane		-17	-8	-7	-6	-1	-11
1-Heptene		-16	-8	-7	-5	-2	-9
Cyclohexane		-6	-5	-5	-4	-1	-7
Cyclohexene			-5	-4	-5	-3	-5
Benzene	-16	-6	-3	-3	-5	-3	-3
Toluene	-17	-7	-3	-4	-5	-3	-4

An ideal solution is characterized by a completely random distribution of solvent and solute molecules. The results mentioned in the preceding paragraph suggest a high degree of ordering for solutions of hydrocarbons in FA and in polyhydric alcohols. Infra-red spectroscopic data of mixtures of hydrocarbons with monohydric alcohols can be interpreted in terms of several species in equilibrium: monomer, cyclic dimers and tetramers, and linear polymers^{18,19}; it is also accepted that FA is a highly associated liquid^{20,21}, although there are discrepancies in the type of association. The possibilities of association obviously increase for polyhydric alcohols, probably leading to the formation of complicated networks.

Equations for regular solutions were deduced by Hildebrand and Wood²² from a statistical model in which thermal motion is sufficient to produce a completely random distribution of solute and solvent molecules. Differences in the interaction energies between like and unlike molecules are taken into consideration in order to account for a non-zero heat of mixing, but the different magnitudes of the forces have no ordering effect on the molecular arrangements, and the entropy of mixing remains ideal. These premises will probably be strictly applicable only to systems that interact exclusively through dispersion forces. However, Blanks and Prausnitz²³ and Gardon²⁴ have extended the theory to polar systems by assuming that the total interaction energies in solution can be expressed as the sum of dispersion, orientation and induction interactions; the non-existence of specific interactions (such as hydrogen bonding) was assumed in both papers.

Later developments in this field have incorporated an hydrogen bonding component to the total solubility parameter²⁵⁻²⁸. A scheme of this type can be very useful to anticipate major trends in chromatographic retention, and constitutes a rational approach to the selection of stationary and mobile phases for the resolution of specific sample mixtures. However, as Karger *et al.*²⁷ have warned, the precision of the final estimates is not expected to be sufficiently adequate as to allow an accurate prediction of the thermodynamic properties of the solution. Any model based on the theory of regular solutions assumes that the entropy of mixing is ideal. This is a critical assumption, and in the case of solutions of hydrocarbons in polyhydric alcohols and FA determines the total inapplicability of the model. In fact, the experimental activity coefficients are very different from those calculated by means of the equations of Karger *et al.* or of Tijssen *et al.*²⁸, employing the values for the specific solubility parameters appearing in their respective tables. A similar disparity between

experimental and calculated gas-liquid partition coefficients was obtained by Karger *et al.*²⁷ for ethanol as solvent or solute.

However, the theory of regular solutions is essentially a model to calculate the heat of mixing, while the activity coefficient is a parameter directly related to the free energy of solution. Assuming that for an hydrocarbon solute all the specific solubility parameters vanish with the exception of the dispersion component, *i.e.*, $\delta^1 = \delta_d^1$, eqn. 3b of Karger *et al.*²⁷ for the transfer energy of one mole of solute from an ideal vapour phase to a very dilute solution takes the form

$$\Delta E^s/\nu_1 = (\delta^2)^2 - 2(\delta_d^2 + \delta_{in}^2)(\delta^1) \quad (9)$$

where ν_1 is the molar volume of the solute, and δ^2 , δ_d^2 and δ_{in}^2 are the total, dispersion and induction solubility parameters of the solvent. Neglecting differences between energies and enthalpies of solution, a plot of $\Delta H_k^s/\nu_1$ against the hydrocarbon solubility parameter should yield a straight line for a given stationary phase, with a slope of $-2(\delta_d^2 + \delta_{in}^2)$ and an intercept of $(\delta^2)^2$.

The results of such a calculation are summarized in Table VI. The total solubility parameters of the hydrocarbons and stationary phases were taken from Hoy's tables²⁹. With the notorious exception of glycerol, to be discussed later, there is a very good correlation for all the stationary phases. However, the square roots of the intercepts are consistently smaller than the stationary phase solubility parameters calculated from the experimental heats of evaporation, the difference increasing with increasing expected association³⁰ in the stationary phase, *i.e.*, GLY > FA > EG > PG > DEG > TEG. This behaviour suggests a picture of the solution process in which the hydrocarbon molecules are accommodated between the chains of associated solvent without extensive breakage or rearrangement of hydrogen bonds. The solvent solubility parameter calculated from the experimental heat of evaporation is too large to be used in eqn. 9 because a substantial portion of the energy taken up in the evaporation process is employed in the disruption of hydrogen bonds, while in the solution process these hydrogen bonds remain unaffected.

The poor correlation obtained for glycerol deserves a comment. First, adsorption at the gas-liquid interface is responsible for most of the retention in glycerol columns; as a consequence, the solution thermodynamic properties are affected by larger errors than are those of the remaining studied solvents. Secondly, as was discussed in the original publication⁴, there are indications that the solution process is more complex in glycerol than in other glycols, with alkanes and olefins probably

TABLE VI

RESULTS OF PLOTS OF EXPERIMENTAL $\Delta H_k^s/\nu_1$ VALUES AGAINST HYDROCARBON SOLUBILITY PARAMETERS FOR SEVERAL STATIONARY PHASES

δ = Stationary phase solubility parameter calculated from latent heats of evaporation and molar volumes.

Stationary phase	δ (cal/ml) ^{1/2}	No. of data points	Intercept (cal/ml)	Slope (cal/ml) ^{1/2}	Correlation coefficient
Glycerol	17.7	14	14.90	- 6.29	0.509
Ethylene glycol	17.0	22	54.62	-13.73	0.975
Propylene glycol	15.0	18	67.29	-16.46	0.981
Diethylene glycol	14.2	21	113.40	-22.04	0.985
Triethylene glycol	13.5	22	133.61	-24.05	0.981
Formamide	19.2	22	53.02	-13.65	0.972

inducing an increase in the solvent ordering, in the form postulated by Frank and Evans³¹ for water as a solvent for hydrocarbons. The case deserves further study by non-chromatographic methods, in order to free the experimental results from the masking action of the adsorption.

The activity coefficient of diisopropyl ether is relatively high for a molecule carrying a functional group susceptible to strong interactions with PG, evidencing a very efficient hindering action of the bulky isopropyl groups. The behaviour of the three chlorinated methanes follows the trend expected from their respective acidities. Thus, the excess enthalpy of solution is zero, within experimental error, for carbon tetrachloride, -0.7 kcal/mol for dichloromethane and -1.4 kcal/mol for chloroform. It is enlightening that the last two solutes, in spite of an exothermic mixing with PG, exhibit positive deviations from Raoult's law.

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